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ROLE OF DELOCALIZED CHARGES IN THE PYROELECTRIC EFFECT (POSTPRINT)

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14. ABSTRACT
We show the temperature dependence of the pyroelectric effect and demonstrate how an increase in dark conductivity as a result of either trap depopulation or proton migration suppresses the pyroelectric-generated high voltage. Electrically shorting crystal z-surfaces coated with a transparent conductive layer is shown to be an effective way of eliminating the breakdown of the surface charge in air. A new method of measuring proton migration temperatures and nonradiative transitions is proposed.

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Role of delocalized charges in the pyroelectric effect

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The temperature dependence of the pyroelectric effect is investigated. An increase in dark conductivity resulting from either trap depopulation or proton migration is shown to suppress the pyroelectric-generated high voltage. Electrically shorting crystal *z* surfaces coated with a transparent conductive layer is shown to be effective in eliminating the breakdown of the surface charge in air and thus provides a means to study weak thermoluminescence in pyroelectric crystals. In addition, a new method to measure proton migration and dark conductivity is proposed; a direct correlation between the emitted light intensity resulting from ionization of air and the pyroelectric current is observed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2234565]

$LiNbO_3$:Fe is a popular ferroelectric material, which is well noted for its photorefractive, photovoltaic, and pyroelectric properties.[1–3] The particular interest of this letter is the pyroelectric effect found in $LiNbO_3$, which can be as large as 1 kV/K for a 1.0 mm thick crystal.[3] The surface charges generated from the pyroelectric field can cause electrical breakdown of the surrounding air, even when under a weak vacuum.

In this letter we show how conductivity from different sources (trap depopulation and proton migration) influences the magnitude of the pyroelectric effect. In addition, an alternative way of studying the temperature dependence of dark conductivity and proton migration in pyroelectric materials is proposed. A method of eliminating the unwanted manifestations of the pyroelectric effect when necessary, as is the cases when detecting weak thermally stimulated luminescence (i.e., weak thermoluminescence), is demonstrated using transparent conductive indium tin oxide (ITO) coatings for electrically shorting the *z* surfaces. This technique is similar to that found in Refs. 4 and 5, where transparent conductive coatings are used to eliminate the effect of photovoltaic breakdown, which is evident in counterpropagating photorefractive two-beam coupling applications. The relationship between the intensity of the light emitted as a result of pyroelectric breakdown (ionization of air) and the pyroelectric current is also investigated.

A congruent $LiNbO_3$:Fe bulk crystal (0.05 mol % Fe_2O_3 and 3.05 mm thick *c* axis) was mounted on the cold finger of a liquid nitrogen Dewar under a weak vacuum (1–10 mtorr), and a cartridge heater, controlled by an Omega temperature controller (Model CN76000), was mounted in the cold finger. A thermocouple fixed directly to the sample monitored the crystal temperature over a range of 143–475 K. The trap states in the host material were populated at a constant temperature of 143 K using Nanolase model NG-1060-100 pulsed doubled Nd:YAG (yttrium aluminum garnet) laser (532 nm, 1 ns pulse width, 4 mW average power, and 1 kHz repetition rate). Immediately after optical excitation, the sample was heated at a linear rate (10 K/min) resulting in thermoluminescence (TL) due to the recombination of thermally activated trapped charges. A photomultiplier tube (PMT) was used for the detection of TL as well as the emission created from the electrical breakdown of air (ionization) due to the buildup and subsequent discharge of the surface charges generated by the pyroelectric field. Data acquisition was achieved by using a Stanford Research Systems series SR200 boxcar integrator, which was interfaced with a computer. The sample was positioned such that the laser light propagated at normal incidence to the surface along the +*c* axis and the detection of luminescence was from the same position (Fig. 1). The pyroelectric current was monitored using a Keithley 6517A electrometer. In order to eliminate the effect of electrical breakdown, when necessary, the sample was prepared with transparent conductive ITO coatings on the *z* surfaces; aquadag (graphite/water mixture) was applied to the surface orthogonal to the *z* surfaces, which was used as a means of electrically shorting these two surfaces (closed-circuit configuration). For the case of pyroelectric current measurements, a thermocouple was used allowing for temperature detection down to 77 K.

Because a large voltage is generated through the pyroelectric effect in $LiNbO_3$:Fe, an accumulated charge buildup at the surface of the crystal can cause a breakdown of the surrounding air at the sample surfaces. Although the sample is held under a vacuum for low temperature measurements, the amount of residual air in the Dewar is sufficient for electrical breakdown to occur given an adequate heating or cooling rate. The presence of sparks is related to the heating/

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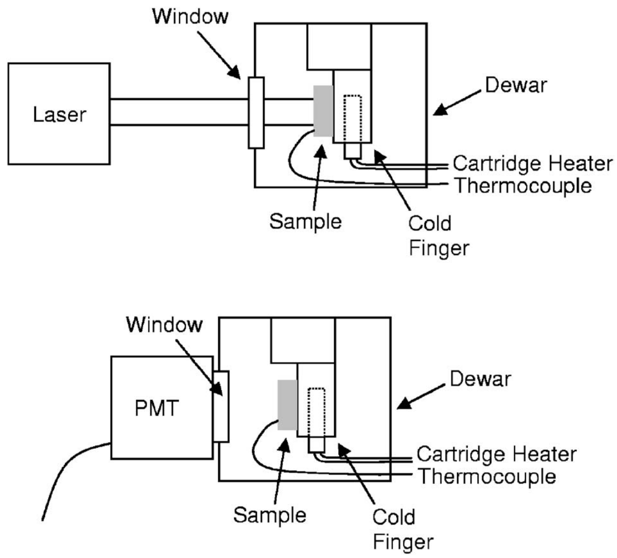

FIG. 1. The experimental arrangement for the initial trap population (top) and luminescence detection (bottom). For measuring the pyroelectric current, an electrometer was used in place of the PMT. Only the bottom portion of the Dewar is shown.

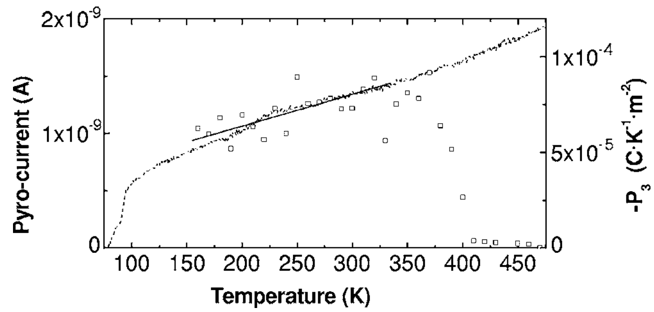

FIG. 3. Temperature dependence of the measured pyroelectric current (left) and the pyroelectric coefficient (right) in an ITO coated $LiNbO_3$:Fe crystal (dashed line). Pyroelectric coefficient was calculated in accord with the temperature ramp rate, 10 K/min, and the area of ITO contacts, 10 $\times$ 10 mm^2. The square symbols are the summed values over 10° increments of the intensity of the sparks (as a result of the ionization of air) in the uncoated crystal as measured in the dark for no initial trap population. A linear fit (solid line) to the summed spark intensities is shown as a guide to the eye in the temperature region (up to 350 K) where the pyrovoltage buildup appears unaffected by the dark conductivity.

cooling rate and the ambient pressure. If the heating/cooling rate is large, the pyroelectric current may be sufficient to overcome the increased conductivity at elevated temperatures and allow surface charge accumulation to generate an electric field causing local arcing. For the thermal cycling rates studied in this work, sparks were not observed in regions of increased conductivity.

A direct result of the electrical breakdown is intense and frequent sparks, causing frequent spikes in the data, Figs. 2(a) and 2(b). Over the measured temperature range (143–475 K) many sparks are observed except over the temperature regions where TL occurs (detrapping) and above 413 K, Fig. 2(a). The temperature regions where there is a reduction/elimination of sparks are attributed to increased levels of dark conductivity. The level of dark conductivity can increase when (1) there is a thermal activation of trap states and the thermally liberated electrons temporarily become delocalized in the conduction band, and (2) an induced proton migration occurs. The proton migration temperatures found in $LiNbO_3$ cover a broad range of values: in Ref. 6 they vary between 120 and 180 °C (393–453 K), in Ref. 7 the thermal fixing of holograms (involving protons) is achieved by heating the sample to 140 °C (413 K), and in Ref. 8 proton migration temperatures are stated to be in the range of 130–140 °C (403–413 K). Such an increase in dark conductivity can provide a mechanism for internal charge leakage, minimizing the buildup of surface charges and in turn electric breakdown. To verify that these suggested mechanisms are plausible for suppressing the buildup of surface charges generated by the pyroelectric effect, the experiment was repeated without any initial population of the trap states, i.e., the traps were completely emptied thermally (at $T > 475$ K). The sample remained in the dark as it cooled down to 143 K and during the subsequent measurement over the temperature range of 143–475 K. The result of the detected emission as a function of temperature is shown in Fig. 2(b).

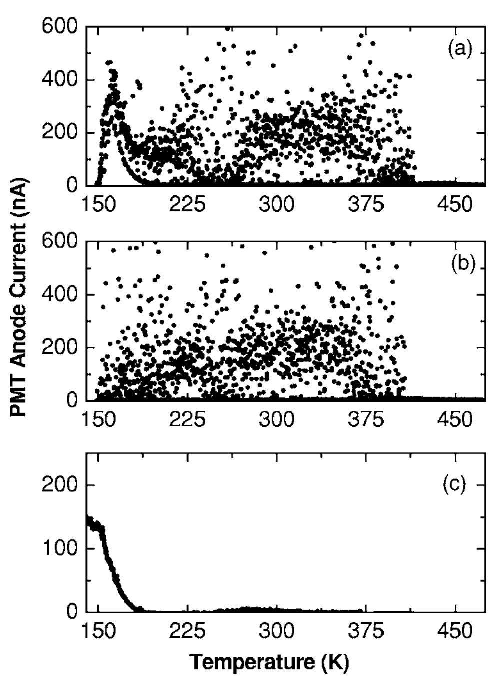

FIG. 2. (a) Temperature dependence of the manifestation of the pyroelectric effect in an uncoated $LiNbO_3$:Fe crystal. (b) The traces were measured in the same manner as in (A), except the traps were not populated with an initial irradiation. (c) Thermoluminescence glowcurve of a $LiNbO_3$:Fe crystal with the z surfaces coated with ITO in a closed-circuit configuration over an extended temperature range.

Comparing the traces in Figs. 2(a) and 2(b), there is an observed reduction of the density of sparks [as seen in Fig. 2(a)] in the region of the TL glowcurve ($T < 200$ K), whereas over this same temperature region in Fig. 2(b), the density of sparks remains fairly constant. It is also seen from Fig. 2(a) that the buildup of the density of sparks corresponds to a weakening of the TL intensity, i.e., reduction in the dark conductivity level. In addition, there appears to be a variation in the density/intensity of the sparks over the observed temperature range, both traces [Figs. 2(a) and 2(b)] exhibit similar trends. In order to understand this trend the intensities of the sparks were summed over 10° increments, without discrimination as to the size of the sparks, and compared to the pyroelectric current as shown in Fig. 3. Although the pyroelectric current was measured as low as 77 K (discussed below), the thermoluminescence and dark conductivity were

only measured as low as 143 K. The sums of the intensities are normalized to the pyroelectric current, and a linear fit to the summed spark intensities is shown as a guide to the eye in the temperature region (up to 350 K) where the pyrovoltage buildup appears unaffected by the dark conductivity. Even though there appears to be some variation in spark density in the Fig. 2, the data of the summed intensities show that below 350 K there is no significant variation in the relationship between the pyroelectric current and the average intensity of the light emission caused by the ionization of the residual air. Not only do these results reveal the influence that the level of dark conductivity has on pyroelectric breakdown, they also identify a technique to verify proton migration temperatures as well as the possibility of nonradiative relaxation of free carriers after their detrapping. Furthermore, it shows a direct relation between the intensity of the sparks and the pyroelectric current.

Coating the samples with conductive transparent ITO on the z surfaces, where the two z surfaces are electrically connected in a closed-circuit configuration, eliminated the electrical breakdown induced luminescence revealing only the weak TL glowcurves, Fig. 2(c). This provides an efficient method to study weak TL from crystals exhibiting a strong pyroelectric effect, where gas discharge emission from electrical breakdown may dominate over the thermally stimulated emission signal. The trace in Fig. 2(c) was taken from a separate study where the trap states were populated at 77 K, which accounts for the slight difference (below 160 K) in thermoluminescence between the traces in Figs. 2(a) and 2(c). For comparison, Fig. 2(c) is plotted using the same temperature scale as in Figs. 2(a) and 2(b). The particular dynamics for the observed TL will be the topic of a future paper.

In order to verify that the reduction in the sparks is associated with an increased dark conductivity and not a reduction in the pyroelectric current at high temperatures, the temperature dependence of the pyroelectric current was measured. The results as measured on an ITO coated $LiNbO_3$:Fe, without the use of aquadag to electrically connect the z surfaces, is shown in Fig. 3 (left). The pyroelectric current increases with temperature, even at temperatures well above the proton migration temperature, indicating the reduction on the pyroelectric field is related to an increase in the dark conductivity. For comparison with published values, the pyroelectric coefficient as a function of temperature is shown in Fig. 3 (right). The measured coefficients are in good agreement with the values from Ref. 9. The affect of conductivity on pyroelectrically induced electrical breakdown may be a reliable and simple new method of measuring the thermal dependence of proton migration and dark conductivity. The gas discharge emission associated with the breakdown of air can be eliminated by electrically shorting the z surfaces. This elimination of the pyroelectric breakdown, and in turn gas discharge emission due to the ionization of air, may improve the signal to noise ratio when detecting weak luminescence from pyroelectric crystals.

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